



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Lubricating Oil Compositions

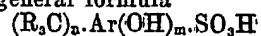
We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a Netherlands Company, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to lubricating oil compositions containing additives suitable for modifying the properties of the lubricating oil.

It is known that the addition of various types of compound to lubricating oils improves various properties thereof, such as their oiliness characteristics, oxidation stability and their detergent action in engines, particularly as manifested in the maintenance of a clean engine during operation. Various compounds which have been used for such purposes include the metal derivatives or organic compounds such as fatty acids, naphthenic acids, alcohols, phenols and ketones. The use of all such additive compounds has resulted in varying degrees of success in obtaining and maintaining maximum operating efficiency.

It is an object of the present invention to provide an improved class of additives for lubricating oils, especially for those lubricating oils which are to be used as crankcase lubricants for internal combustion engines, which additives exhibit the desirable properties of promoting oxidation stability and general engine cleanliness, reducing ring sticking and piston varnish formation, and improving the film strength of the lubricating oil.

Accordingly the present invention provides a lubricating oil composition comprising a lubricating oil and a minor proportion of an oil-soluble polyvalent metal basic salt of a sulphonic acid having the general formula



[Price 2/8]

Price 3s. 6d.

wherein Ar is an aromatic hydrocarbon radical, which may be partially hydrogenated and/or alkylated, provided no tertiary carbon atom is present in the alkyl radical, the R's are the same or different alkyl radicals which do not contain a tertiary carbon atom, n is 1, 2, 3 or 4 and m is 0, 1, 2 or 3, the sum of m and n not exceeding the number of valencies of the radical Ar which are available for bearing substituent groups.

The aforesaid oil-soluble sulphonates are generally used in an amount of 0.05 to 10%, an amount of 0.2 to 1.5% being preferred. These percentages are by weight, based upon the whole composition.

The oil-soluble sulphonates suitable for use in the compositions of the present invention may be derived from various polyvalent metals. Particularly suitable sulphonates are those derived from the alkaline earth metals, e.g., calcium, magnesium, strontium and barium. However, they may be derived from other metals, such as aluminium, iron, tin, zinc, cadmium, indium, cobalt and nickel.

The oil soluble sulphonates of the present invention may be prepared from various aromatic compounds including benzene and its various alkyl derivatives, such as the xylenes (ortho-, meta- and para-xylene) ethyl benzene, styrene, durene, hemimellitene and cumene, the various polynuclear aromatic hydrocarbons, such as naphthalene and anthracene and their alkyl derivatives, and phenols, which may be monocyclic or polycyclic and monohydric or polyhydric and which may be alkyl and/or aryl substituted, such as *o*-cresol, xylenol, alpha- and beta-naphthol and the mono-, di- and tri-hydroxy benzenes, e.g., phenol and catechol. Under some circumstances a crude commercial product containing substantial quantities of phenol, for example, the crude phenol fraction obtained in the by-product distillation of coal, may be used. Similarly, partially

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hydrogenated aromatic compounds as well as their alkyl derivatives may be used, e.g., tetralin. Also a solvent extract such as a sulphur dioxide extract, of a petroleum fraction of the kerosine boiling range, which contains a suitable amount of aromatic hydrocarbons, may be used.

From these aromatic compounds the oil soluble sulphonates suitable for use in the compositions of the present invention can be prepared by alkylating the aromatic compound to introduce into it one or more alkyl groups R_3C , sulphonating this alkylation product, and converting the sulphonic acid thus obtained into one of its polyvalent metal basic salts.

The alkylation is preferably carried out with isobutylene or a polymer thereof or with a mixture of the same. The alkylation product may contain principally tert.-butyl groups, as well as alkyl groups derived from isobutylene dimers, trimers tetramers or higher polymers, or mixtures of the same, as the alkyl groups attached to the aromatic nucleus, since, dependent upon the alkylation conditions, considerable polymerisation and depolymerisation of the alkylating agent may occur.

The following description of the preparation of basic calcium tert.-butyl naphthalene sulphonate is an example of the preparation of oil-soluble sulphonates suitable for use in the compositions of the present invention.

Naphthalene is alkylated with isobutylene or di-isobutylene in the presence of $AlCl_3$ or H_2SO_4 or any of the other well known alkylation catalysts. The reactants are used in such proportions than on an average between 3 and 4 tertiary butyl groups are introduced into the naphthalene molecule. After washing the reaction mixture to remove the catalyst therefrom, the alkylation product, the desired tert.-butylnaphthalene, is recovered as an appropriate distillate fraction.

Sulphonation of this butylated naphthalene is carried out in the following manner, the parts referred to being parts by weight except where otherwise stated, the relation of parts by weight to parts by volume being that of the kilogram to the litre. Into suitable reaction vessel fitted with a stirrer, a dropping funnel and a condenser which is cooled with solid CO_2 , is placed 444 parts of the butylated naphthalene, 300 parts of carbon tetrachloride and 1500 parts by volume of liquid sulphur dioxide. The material is slowly stirred and over a period of 15

minutes there is added a solution of 120 parts of sulphur trioxide ("Sulfan B." a stabilised sulphur trioxide sold by General Chemical Co.) in 500 parts by volume of liquid sulphur dioxide. After refluxing at $-80^\circ C.$ for two hours, the reaction mixture is allowed to warm up to room temperature, whereby part of the sulphur dioxide evaporates from the mixture. After standing overnight the residue is treated with 500 parts by volume of water and slowly heated to boiling. This removes the remaining sulphur dioxide and the carbon tetrachloride. To this material is now added 50% Bé aqueous NaOH until it is neutral. After evaporating to dryness the residue is treated with benzene to dissolve the organic material present in the residue. The inorganic salts present in the residue are substantially insoluble in benzene and are removed by filtration of the solution. The filtrate is concentrated and the residue dried at $100^\circ C.$ at 3—5 mm. pressure. There remains 524 parts of the sodium sulphonate product, an analysis of which indicates that it contains 81.9% of the sodium sulphonate and 11.0% of hydrocarbon with small amounts of inorganic salts and other impurities. The resulting sodium salt of the butylated naphthalene sulphonic acid is then treated with calcium chloride and calcium hydroxide to produce the corresponding basic calcium salt.

In a similar manner, employing isobutylene or polymers thereof as alkylating agent, various other alkylation products can be prepared, for example di-octyl phenol, tetrabutyl naphthalene, di-dodecylphenol, di-dodecyl naphthalene, di-dodecyl benzene and various other derivatives of phenols, benzene, naphthalene or tetralin substituted with butyl groups. In these products the butyl groups can be considered to be derived from isobutylene (so they are tert.-butyl groups) and in the same way the octyl and dodecyl groups can be considered to be derived from the dimer and trimer of isobutylene respectively. These alkylation products can be sulphonated to produce sulphonic acids therefrom and these sulphonic acids can be converted into their polyvalent metal basic salts, such as the basic calcium salts.

The basicity (in %) of the basic calcium sulphonates is generally less than 50%, and is usually between about 40% and about 20%. The basicity is defined as

Per cent. basicity = $\frac{\text{equivalents of basicity}}{100 \text{ gms.}}$

$\frac{\text{equivalents of total metal}}{100 \text{ gms.}}$

The basicity of the sulphonates arises from the unreacted calcium hydroxide contained therein and/or from the formation of monohydroxy calcium sulphonates.

- 5 The lubricating oils which can be used in the compositions of this invention may be mineral lubricating oils obtained by distillation from paraffinic, naphthenic, asphaltic or mixed base crudes. If desired, various blended oils may be employed as well as residuals, particularly those from which the asphaltic constituents have been removed. The oils may be refined by the conventional methods using acid, alkali, clay or other agents, such as aluminium chloride, or they may be extracted oils produced, for example, by solvent extraction with selective solvents such as phenol, cresols, sulphur dioxide, furfural, dichloro-ethyl ether, nitrobenzene, crotonaldehyde and sulpholane. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerisation of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracked coal tar fractions and coal tar or shale oil distillates may also be used. Also for special applications various organic esters or animal, vegetable or fish oils or their hydrogenated, polymerised or voltolised products may be employed, either alone or in admixture with mineral oils.
- 35 For the best results the base stock chosen should normally be that oil which, without the additives of the present invention, gives the optimum performance in the service contemplated. However, since one advantage of the additives of the present invention is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually have a viscosity of from about 40 to 150 seconds Saybolt at 210° F.
- 60 For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a viscosity at 210° F., of 45 to 90 seconds

Saybolt and a viscosity index of 0 to 50. However, in certain types of Diesel engines, particularly in high speed Diesel engines, and in aviation and other gaso-
line engines, oils of higher viscosity index are often preferred, for example, oils having viscosity indices of from 75 to 100, or even higher.

In order to demonstrate the superiority of lubricating oil compositions containing the oil-soluble polyvalent metal basic sulphonates according to the present invention, over various other lubricating oil compositions the oxidation stability of these compositions was determined in the well known Thrust Bearing Corrosion and Oxidation Test at 120° C. with a copper-lead bearing catalyst. A description of the test apparatus employed is given in the National Petroleum News, September 17, 1941, pp. 294-296.

The various compositions tested all consisted of the same lubricating oil and a calcium sulphonate in an amount of 0.5% by weight determined as sulphate ash. For purposes of comparison the lubricating oil was also tested without any additive. The lubricating oil was obtained from a mixture of Poso and Coalinga California naphthenic crudes by vacuum distillation, extraction with furfural, mild chemical treatment with sulphuric acid and filtering through clay. The finished oil had the following properties:

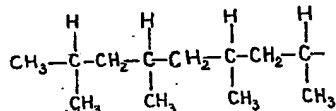
| | | | | |
|------------------------------|---|---|------|-----|
| Gravity, °API | - | - | 25.3 | 100 |
| Colour, A.S.T.M. | - | - | 1-½ | |
| Pour Point, °F. | - | - | -20 | |
| Flash, C.O.C., °F. | - | - | 430 | |
| Fire, °F. | - | - | 480 | |
| Viscosity, S.U.S. at 100° F. | - | - | 630 | 105 |
| Viscosity index | - | - | 50 | |

Because the oxidation times were very different for the various compositions tested, a valid comparison of the corrosion could not be made. However, a comparison of the quantities of oxygen absorbed was possible and the test results are shown in Table A.

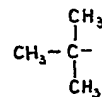
The compositions tested were the following:

1. Base oil
2. Base oil and basic calcium dinonyl naphthalene sulphonate
3. Base oil and basic calcium di-dodecyl naphthalene sulphonate 120
4. Base oil and basic calcium di-dodecyl phenol sulphonate
5. Base oil and basic calcium dodecyl benzene sulphonate 125
6. Base oil and basic calcium sulphonate, derived from tetralin, substituted with an alkyl group having 18 carbon atoms
7. Base oil and basic calcium petroleum sulphonate 130

8. Base oil and basic calcium tetra-tert. butyl naphthalene sulphonate
9. Base oil and basic calcium dioctyl phenol sulphonate.
- 5 In compositions 3, 4 and 5 the dodecyl groups of the sulphonate were derived from a propylene tetramer and in composition 2 the nonyl groups of the sulphonate were derived from a propylene trimer. In composition 9 the octyl groups of the sulphonate were derived from an isobutylene dimer. Compositions 8 and 9 thus contain additives in accordance with the present invention. In these additives the aromatic radical is substituted with alkyl groups which do not contain a tertiary carbon atom and have the general formula R_3C , i.e. they are attached to the aromatic radical through a quaternary carbon atom. The additives of compositions 2, 3, 4, 5 and 6 on the other hand contained aromatic radicals substituted with alkyl radicals which do not conform to these requirements. The test results obtained from the base lubricating oil and the base oil plus a commercial grade of basic calcium petroleum sulphonate are set forth for purposes of comparison.
- It follows from Table A that compositions 2, 3, 4, 5 and 6 are considerably more susceptible to oxidation than compositions 8 and 9. The reason for this difference in stability is considered to be a function of the hydrogen atoms attached to tertiary carbon atoms present in the alkyl groups attached to the aromatic radicals. For example, a propylene tetramer group

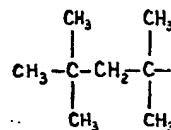


has four such hydrogen atoms which are vulnerable to attack by oxygen whereas the tertiary butyl group



has none.

Similarly the diisobutylene (isobutylene dimer) group such as



has none.

The above is borne out by the greatly improved performance of a lubricating oil composition containing basic calcium dioctyl phenol sulphonate (in which the octyl groups are derived from an isobutylene dimer) as compared with a similar oil composition containing basic calcium di-dodecyl phenol sulphonate (in which the dodecyl radicals are derived from a propylene tetramer). Furthermore, a similar improvement is exhibited by a lubricating oil composition containing basic calcium tetra-tert.-butylnaphthalene sulphonate as compared with lubricating oil compositions containing basic calcium di-dodecyl naphthalene sulphonate (in which the dodecyl radicals are derived from a propylene tetramer) or basic calcium di-nonyl naphthalene sulphonate (in which the nonyl radicals are derived from a propylene trimer).

TABLE A

| Sulphonate | | T.B.O. and O. Test Results. 120° C., Cu — Pb Bearing Catalyst | | | | |
|------------|--|--|---|---|--|--|
| | Description | Per cent* Basicity | 250 ml. O ₂ absorbed Time, Hours | 750 ml. O ₂ absorbed Time, Hours | 1500 ml. O ₂ absorbed Time, Hours | Bearing Loss mg./cm. ² (Total O ₂ absorbed in ml.) |
| 1. | None (Base oil only) | — | 10.2 | 26.4 | 69.9 | 0.35 (1580) |
| 2. | Basic calcium dinonyl naphthalene sulphonate | 36 | 32.4 | 33.1 | 35.2 | 22.6 (2050) |
| 3. | Basic calcium didocyl naphthalene sulphonate | 18 | 21.1 | 22.6 | 28.1 | 16.8 (1580) |
| 4. | Basic calcium didodecyl phenol sulphonate | 45 | 38.0 | 59.3 | 63.8 | 19.7 (1775) |
| 5. | Basic calcium dodecyl benzene sulphonate | 40 | 20 | 20.7 | 22.4 | 8.8 (1580) |
| 6. | Basic calcium sulphonate, derived from tetralin, substituted with a hydrocarbon radical having 18 carbon atoms | 41 | 26.3 | 27.8 | 31.7 | 9.0 (1675) |
| 7. | Commercial basic calcium petroleum sulphonate | 26.5 | 31.5 | 32.2 | 34.2 | 23.75 (1950) |
| 8. | Basic calcium tetra-tert-butyl naphthalene sulphonate | 23 | 102.5 | 105.5 | 110.4 | 13.3 (1625) |
| 9. | Basic calcium dioctyl phenol sulphonate | 80 | 123.8 | 215.6 | 223.1 | 21.1 (2200) |

*Per cent Basicity = $\frac{\text{equivalents of basicity/100 grams}}{\text{equivalents of total metal/100 grams}}$

As shown by the data in Table A, particularly outstanding oxidation stability is shown by those oil compositions which contain sulphonates according to the invention, specifically the basic calcium dioctylphenol sulphonate and the basic calcium tetra-tert.-butyl-naphthalene sulphonate.

- Furthermore, in order to demonstrate the usefulness of lubricating oil compositions containing sulphonates according to the invention, a number of CRC L—3 engine tests were performed employing two different basic calcium sulphonates (viz., commercial basic calcium petroleum sulphonate and basic calcium tetra-tert.-butyl-naphthalene sulphonate) as additives to the oil used as the crankcase lubricant. The base oil employed was the lubricating oil described above. The amount of the sulphonates present in the compositions was 0.5%, determined as sulphate ash based on the whole composition. For purposes of comparison the lubricant without any sulphonates being present was also tested. The fuel employed in these engine tests was a fuel of a low sulphur content. The test involved the operation of a special four-cylinder diesel test engine (Caterpillar 4 cylinder diesel test engine, $4\frac{1}{4}$ " bore \times $5\frac{1}{2}$ " stroke). After a 6-hour break-in run, this engine was run for the test period at fixed speed and load, with the test oil as a lubricant. The test conditions were:

Engine speed: 1400 ± 14 r.p.m.

Engine load: 37 b.h.p.

Jacket outlet coolant temperature: $200 \pm 2^\circ\text{F}$.

- Oil temperature to bearings: $212 \pm 2^\circ\text{F}$.

Intake air temperature: $140 \pm 5^\circ\text{F}$.

- After the test period the pistons were examined for the amount of lacquer formed thereon. The results of these tests are given in the accompanying drawing, in which the amount of lacquer formed on the piston is plotted against the time, in hours, during which the compositions were tested. The amount of lacquer on the piston is expressed by a number, the highest number (10) being allotted to a clean piston.

- As shown by the accompanying drawing, the lubricating oil composition containing basic calcium tetra-tert.-butyl-naphthalene sulphonate maintained a clean engine for a period of operation of about 110 hours and thus showed a considerable improvement over the composition containing commercial basic calcium petroleum sulphonate.

In addition to the additives of the

present invention, the lubricating oil compositions may contain minor amounts of other additives such as dyes, pour point depressors, sludge dispersers, foam suppressing agents, antioxidants, thickeners, viscosity index improvers and oiliness agents. Suitable members of these classes of compounds include heat-thickened fatty oils, sulphurised fatty oils such as sulphurised sperm oil, organic metallic compounds, soaps, resins, such as polymerised lauryl methacrylate, rubber, olefin polymers such as polyisobutylene, voltolised fats such as voltolised sperm oil, voltolised mineral oils, voltolised waxes, colloidal solids, such as graphite or zinc oxide, and sulphurised wax olefins. Additional examples of suitable additives comprise dibenzyl disulphide, phenyl alpha naphthylamine, diamyl trisulphide, tricresyl phosphate, 2,6-ditert.-butyl-4-methyl phenol, and the reaction product of phenol with diisobutylene treated with sulphur chloride.

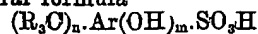
A class of additives of particular importance is constituted by the additives which serve to enhance the detergent and sludge dispersive qualities and aid the solubility of the metal sulphonate additives of the present invention and at the same time impart some oiliness properties to the lubricating oil compositions. These additives will hereinafter be referred to as solubilising agents. Many types of compounds may be used for this purpose, and they include esters, ketones, alcohols, thioalcohols, amines, aldehydes and halogenated or nitrated compounds.

Solubilising agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight or branched-chain aliphatic alcohols, such as octyl alcohol ($\text{C}_8\text{H}_{17}\text{OH}$), lauryl alcohol ($\text{C}_{12}\text{H}_{25}\text{OH}$), cetyl alcohol ($\text{C}_{16}\text{H}_{33}\text{OH}$), stearyl alcohol ($\text{C}_{18}\text{H}_{37}\text{OH}$) and heptadecyl alcohol ($\text{C}_{17}\text{H}_{35}\text{OH}$), the corresponding olefinic alcohols, such as oleyl alcohol, alicyclic alcohols, such as naphthenic alcohols, and alcohols containing aromatic groups, for instance, phenyl-octyl alcohol and octadecylbenzyl alcohol or mixtures of these various alcohols. They may be pure or substantially pure synthetic alcohols, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e.g., paraffin wax or petrolatum. However, certain mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil alcohol may be used. Although it is preferable to isolate the alcohols from

those natural materials, for some purposes the wool fat, sperm oil or other natural products rich in alcohols may be used *per se*. Other suitable solubilising agents include stearyl nitrile and stearylamine.

What we claim is:—

1. A lubricating oil composition comprising a lubricating oil and a minor proportion of an oil-soluble polyvalent metal basic salt of a sulphonic acid having the general formula



wherein Ar is an aromatic hydrocarbon radical which may be partially hydrogenated and/or alkylated provided no tertiary carbon atom is present in the alkyl radical, the R's are the same or different alkyl radicals, which do not contain a tertiary carbon atom, n is 1, 2, 3 or 4, and m is 0, 1, 2 or 3, the sum of m and n not exceeding the number of valencies of the radical Ar which are available for bearing substituent groups.

2. A lubricating oil composition as claimed in claim 1, in which the oil-soluble polyvalent metal basic salt of the sulphonic acid is an alkaline earth metal salt

3. A lubricating composition as claimed in claim 2, in which the alkaline earth metal is calcium.

4. A lubricating oil composition as claimed in any one of the preceding claims, in which the R_3O groups are derived from isobutylene or a polymer thereof.

5. A lubricating oil composition as claimed in any one of the preceding claims, in which the aromatic hydrocarbon radical Ar is polycyclic.

6. A lubricating oil composition as claimed in claim 5, in which the aromatic hydrocarbon radical Ar is a naphthalene radical.

7. A lubricating oil composition as claimed in claim 6, in which the oil-soluble polyvalent metal basic salt of the sulphonic acid is basic calcium tetra-tert-butyl-naphthalene sulphonate.

8. A lubricating oil composition as claimed in any one of claims 1 to 4, in which the aromatic hydrocarbon radical Ar is monocyclic.

9. A lubricating oil composition as

claimed in claim 8, in which the oil-soluble polyvalent metal basic salt of the sulphonic acid is basic calcium dioctyl phenol sulphonate in which the octyl groups are derived from diisobutylene.

10. A lubricating oil composition as claimed in any one of claims 1 to 4, in which the aromatic hydrocarbon radical Ar is derived from aromatic hydrocarbons obtained by solvent extraction of a petroleum fraction of the kerosine boiling range.

11. A lubricating oil composition as claimed in any one of the preceding claims, in which the oil-soluble polyvalent metal basic salt of the sulphonic acid is present in an amount of 0.05 to 10% by weight, based upon the whole composition.

12. A lubricating oil composition as claimed in any one of the preceding claims, in which the oil-soluble polyvalent metal basic salt of the sulphonic acid is present in an amount of 0.2 to 1.5% by weight, based upon the whole composition.

13. A lubricating oil composition as claimed in any one of the preceding claims, containing additionally a minor amount of a solubilising agent.

14. A lubricating oil composition as claimed in claim 13, in which the solubilising agent is an alcohol having 8 or more carbon atoms.

15. A lubricating oil composition as claimed in any one of the preceding claims, containing additionally a minor amount of a dye, pour point depressor, sludge disperser, foam suppressing agent, anti-oxidant, thickener, viscosity index improver and/or oiliness agent.

16. A lubricating oil composition as claimed in any one of the preceding claims, in which the lubricating oil is a mineral lubricating oil.

17. Lubricating oil compositions containing oil-soluble polyvalent metal basic salts of a sulphonic acid of the general formula set out in claim 1 substantially as hereinbefore described.

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709.587 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

